

# **LARGE AREA SILICON CONE ARRAYS FABRICATION AND CONE BASED NANOSTRUCTURE MODIFICATION**

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## **FIELD OF THE INVENTION**

The present invention relates to the fabrication and further modification of material nano-structures, which have great potential in field emission applications.

## **BACKGROUND OF THE INVENTION**

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Since the discovery of cone-like structures on an ion bombarded glow discharge cathode by Guenther Schulze and Tollmien (Z. physik 119, p.685, 1942), surface texturing of various materials has aroused great interests. One of the most important applications of the textured surfaces is related to their field emission related properties. Arrays of cones or pyramids have been successfully used in field desorption mass spectroscopy (Beckey et. al, J. Phys. E. 12, p72, 1979). They also have potential to be used as the electron source of ultrahigh vacuum gauges and gas analyzers.

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In spite of the above advantages, cone-like arrays have not been used extensively, mainly due to the difficulties which are involved in their production.

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Various techniques have been used to fabricate the cone-like structures for decades. Beckey et al. (J. Phys. E. 12, p72, 1979) have used a two-step method to grow dense arrays of metallic needle crystals on a cathode of a vacuum diode. However, this method involves a fairly complicated process, and a very limited number of metals can be fabricated this way. Whitton et al. (Appl. Surf. Sci. 1, p408, 1978) have reported copper cone formation after a bombardment dose of  $10^{19}$  Ar ions/cm<sup>2</sup> during chemical vapor deposition (CVD) growth. This method is fairly effective for most of the metals, however, materials such as silicon and germanium can not be fabricated

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by this method. Several other growth-induced cone formations have also been reported, including hot filament CVD growth (Chen et al., J. Crystal. Growth, 210, p527, 2000), and Vapor-Liquid-Solid (VLS) technique, in which  $\text{SiCl}_4$  and  $\text{H}_2$  are used as the vapor phase (Kiselev et al., Micron 28, p21, 1997). These methods are, however, only effective for one or two types of materials.

Ion beam techniques are widely employed for the purpose of surface texturing. Various materials systems have been investigated (Hudson et al., J. Vac. Sci. Technol., Vol 14, p286, 1977; Floro et al., J. Vac. Sci. Technol., A(1) 3, p1398, 1983; Fujimoto et al., J. Appl. Phys. 77, p2725, 1994; Okuyama et al., Surf. Sci. 338, pL857, 1995). All of them have been able to fabricate the cone-like structures. However, the fabricating area are usually small, the cone-like arrays are not uniform, and the array density is not high. Seeger et al. (Appl. Phy. Lett. 74, p1627, 1999) have developed a method using rough metal films as plasma etching masks, which is able to produce fine silicon cones or pillar-like structures with controllable array density. Their method, however, involves mask-making and the use of poisonous gas such as  $\text{SF}_6$ , which implies increased cost and environmental problems.

## SUMMARY OF THE INVENTION

It is the object of the present invention to provide one-step methods for fabricating large area uniform silicon cone arrays with various cone morphologies, cone surface modification for field emission applications, and cone-based nano-structure modifications.

The silicon cone array can be prepared by ion-beam sputtering using an ion source in a high vacuum chamber. Metal catalysts may be provided to enable the cone formation. The substrate and metal catalyst should be arranged in a specific

configuration to ensure the uniformity of the as-synthesized cone arrays over a large area. The present invention further provides apparatus for ion-beam synthesis of silicon cone arrays, comprising a high vacuum chamber suitable for ion-beam sputtering, a means for holding a substrate in the chamber and a means for arranging  
5 the metal catalyst around the substrate.

The field emission properties of the as-synthesized cone arrays can be improved by several surface modification methods, including acid etching, annealing and low work function metal coating.

Silicon and silicon oxide nanowires can be grown from the tips of individual  
10 cones. The nanowires on the tips of the cones can be prepared using a hot filament chemical vapor deposition chamber. Argon is used as a protective gas, and hydrogen is used as reductive gas in order to achieve the silicon nanowires. The present invention provides apparatus for nanowire growth, comprising a chemical vapor deposition chamber, means for holding a substrate in the chamber, and means for  
15 supporting one or more filaments in the chamber. The deposition time is strictly controlled to enable one nanowire-one cone tip relationship.

### BRIEF DESCRIPTION OF THE DRAWINGS

Some embodiments of the invention will now be described by way of example  
20 and with reference to the accompanying drawings, in which  
FIG. 1 is a schematic diagram of the apparatus according to an embodiment of the present invention,  
FIG. 2 is a schematic diagram of the apparatus according to an embodiment of the present invention,

FIG. 3 is a scanning electron microscope (SEM) micrograph of the silicon cone arrays, corresponding to example A ,

FIG. 4 is an energy dispersed x-ray (EDX) spectrum corresponding to the silicon cone image inserted in the left, which is taken from FIG. 3,

5 FIG. 5 is a current- voltage (I-V) plot of the silicon cones shown in FIG. 3,

FIG. 6 is a SEM micrograph of the silicon cone arrays, corresponding to example B,

FIG. 7 is an EDX spectrum corresponding to the silicon cone image inserted in the left, which is taken from FIG. 6,

FIG. 8 is a SEM micrograph of the silicon cone arrays, corresponding to example C,

10 FIG. 9 is an EDX spectrum corresponding to the silicon cone image inserted in the left, which is taken from FIG. 8,

FIG. 10 is a transmission electron microscopy (TEM) image of one silicon cone, corresponding to example C,

FIG. 11 is a transmission electron diffraction (TED) pattern of the silicon cone shown

15 in FIG. 10, (a), (b), (c) and (d) corresponds to areas marked in FIG. 10,

FIG. 12 is a cross-sectional SEM micrograph of silicon cone arrays, corresponding to example D,

FIG. 13 is a cross-section SEM micrograph of the silicon cone arrays, corresponding to example A,

20 FIG. 14 is a SEM micrograph of the silicon cone arrays, corresponding to example E,

FIG. 15 is a I-V plot of the silicon cones shown in FIG. 14,

FIG. 16 is a SEM micrograph of the silicon cone arrays, corresponding to example F,

FIG. 17 is a I-V plot of the silicon cones shown in FIG. 16,

FIG. 18 is a SEM micrograph of the silicon cone arrays, corresponding to example G,

25 (a) as-synthesized cones; (b) cones after hydrofluoric etching for 3 minutes,

FIG. 19 is a I-V plot of the silicon cones shown in FIG. 17 (b),

FIG. 20 is a I-V plot of the silicon cones, corresponding to example H,

FIG. 21 is a SEM micrograph of a silicon oxide nanowire grown on the tip of a silicon cone, corresponding to example I,

5 FIG. 22 is a TEM image of the silicon oxide nanowire shown in FIG. 21,

FIG. 23 is a TED pattern of the silicon oxide nanowire shown in FIG. 22,

FIG. 24 is an electron energy loss spectroscopy (EELS) spectrum of the silicon oxide nanowire shown in FIG. 22, (a) silicon K edge; (b) oxygen K edge, and

10 FIG. 25 is TED pattern of the silicon nanowires, which are grown on the tips of silicon cones, corresponding to example J,

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1, an ion-beam deposition reactor 100 is shown. Reactor 100 consists of a high vacuum chamber 101; an ion source 102, which can be either a rf ion source or a Kaufman gas ion source; a substrate holder 103 for supporting the substrate and the metal catalysts, and a halogen lamp 104 for substrate heating. The substrate holder 103 consists of a multifunctional feed-through 105 and a holder clamp 106. The multifunctional feed-through 105 makes the substrate holder rotatable so that the incident angle of the ion beam can be varied from 0 to 90 degree. The holder clamp 106 can be made of various metals consistent with the metal catalysts used, preferably nickel, molybdenum and tungsten.

The ion-beam reactor 100 further comprises an inlet 107 for a sputtering gas, which is circulated through the chamber 101 by a turbo-molecular pump 108 and a mechanical pump 109. An ion gauge 110 and a cold cathode gauge 111 are provided for monitoring the pressure of the sputtering gas in chamber 101.

A suitable silicon substrate 201 is mounted in the center of the substrate holder clamp 106. The metal catalyst 202, which can be nickel, molybdenum, tungsten etc., is shaped into thin flat foil and mounted around the substrate 201. Silicon substrate is used in the present invention in order to achieve silicon cone arrays. Other materials  
 5 such as germanium, copper, graphite, and the like., can be used as the substrate to obtain cones made of the respective substrate of germanium, copper or graphite.

The fabrication of cone arrays is carried out by argon ion sputtering, while the argon ions are generated from the ion source. The argon gas pressure is controlled at  $2 \times 10^{-4}$  Torr. Argon is one possible sputtering gas that may be used with the present  
 10 invention, other gases such as helium, neon, xenon, or hydrogen etc. are equally possible. The ion energy used in the present invention ranges from 100 eV to 1000 eV. The incident angle of the ion-beam varies from 0 to 90 degree, the substrate temperature varies from 100C to 600C, and the fabrication time varies from 30 minutes to 4 hours for each individual process.

15 The formation of the cone structures probably involves the following process: Metal catalysts are sputtered off from the bulk materials and re-deposited onto the silicon substrate, forming a certain alloy with the substrate material. The alloy is relatively stable to ion-sputtering, therefore protects the substrate material underneath from ion etching and leads to the cone steady-state evolution. As a result,  
 20 large area uniform cone arrays are formed, with the individual cone consisting of a cone body made of the substrate material and a cone head made of the metal catalyst and metal/substrate alloys.

Surface modification of the as-synthesized cone for field emission applications can be done in several ways. As an example, the as-synthesized Si cones on a Si  
 25 substrate can be dipped into 5% hydrofluoric (HF) acid upside down for 3 minutes,

using plastic tweezers and a clamp. As silicon and silicon oxide are etched away, other impurities on the cone surface fall into the hydrofluoric acid as well, resulting in a fine cone tip and clean cone surface. A 5% concentration is used with the present embodiment of the invention, HF acid at other concentrations (1%--48%) can be  
 5 equally effective. The etching time can be different from sample to sample, usually in the range of 10 seconds to 10 minutes. Acid mixtures of HF, HNO<sub>3</sub>, HCl, or H<sub>2</sub>SO<sub>4</sub> are equally possible for the same purpose as stated in the present invention.

Annealing under ultra-high vacuum conditions is another possible method for cone surface modification in the present invention. The annealing temperature ranges  
 10 from 100°C to 800°C, and the annealing time is between 10 to 30 minutes. An ultra-high vacuum chamber is required for this method.

Another effective method for cone surface modification is low work function material coating on the cone surface. Cesium is chosen to be deposited on the cone surface in the present embodiment of the invention. Other low work function metals  
 15 are possible for the different samples. For the deposition of Cesium, an ultrahigh vacuum chamber is required. The thickness of the Cesium layer ranges from 10 –100 angstroms.

Turning to FIG.2, a chemical vapor deposition (CVD) reactor 400 is shown. Reactor 400 consists of a CVD chamber 401, two feed-throughs 402 for supporting  
 20 one or more filaments, a substrate holder 403 for supporting the substrate, and a heater 404 for substrate heating. The CVD reactor 400 further comprises an inlet 405 for protective or reductive gas, which is passed through chamber 401 by means of pump 406. A pressure gauge 407 is provided for monitoring the pressure of the reactant gas in the chamber 401.

The growth of the silicon oxide nanowires on the tips of the cones is realized at a pressure of 15-25 Torr and 900-950°C substrate temperatures for 5-10 minutes. The protective gas used in the present embodiment of the invention is argon, though other inert gas such as helium, neon, and xenon are equally possible. The growth of silicon nanowires is achieved by adding hydrogen gas, which probably decomposes to atomic H near the hot filament at temperatures higher than 1800°C. The atomic hydrogen acts as a reductant to prevent the growing silicon nanowires from oxidation. The ratio between argon and hydrogen is 9 to 1 in the present embodiment of the invention, though other gas ratios can be equally effective. CVD using hot filament excitation techniques is one possible technique that may be used with the present invention, others such as microwave, rf or dc plasma source are as well effective.

### EXAMPLES

The following examples are presented for a further understanding of the invention.

#### Example A

The silicon cone array for this sample was prepared in the apparatus shown in FIG. 1. Mirror polished silicon was used as the substrate. Nickel was used as the metal catalyst. The substrate temperature was maintained at 550°C. Argon was used as the sputter gas and the total pressure was kept at  $2 \times 10^{-4}$  Torr. The ion energy was chosen at 900eV and ion-current was 40 mA. The angle between the center ion-beam and the substrate surface normal is kept at 20 degree. The ion-sputtering time is 120 minutes.



Scanning Electron Microscopy (SEM) micrographs of the above sample are shown in FIG. 3. The 1cm x 2cm silicon substrate is covered with uniform silicon cone arrays. The density of the cones is measured as  $10^8/\text{cm}^2$ . The height of each cone is up to several microns and the lateral size of the cone tip ranges from tens of nanometers to hundreds of nanometers. The contrast of the cone body and cone tip appears to be different, suggesting different chemical contents. Energy-dispersed x-ray (EDX) microanalysis shows that the cone body is composed of silicon and the cone tip is composed of silicon and nickel (FIG. 4). FIG. 5 shows the current-voltage (I-V) characteristics plot of the as-synthesized sample. The turn-on field, which is defined as the electric field leading to a current density of  $0.01 \text{ mA}/\text{cm}^2$ , is  $34 \text{ V}/\mu\text{m}$ .

#### Example B

The silicon cone array for this sample was prepared under the same experimental conditions as example A, except that tungsten was used as the metal catalyst.

SEM micrographs of the above sample are shown in FIG. 6. The 1cm x 2cm silicon substrate is covered with uniform silicon cone arrays. The density of the cones is measured as  $10^8/\text{cm}^2$ . The height of each cone is up to several microns and the lateral size of the cone tip ranges from tens of nanometers to hundreds of nanometers. The contrast of the cone body and cone tip appears to be different, suggesting different chemical contents. EDX microanalysis shows that the cone body is composed of silicon and the cone tip is composed of silicon and tungsten (FIG. 7).

### Example C

The silicon cone array for this sample was prepared under the same experimental conditions as example A, except that molybdenum was used as the metal catalyst.

5 SEM micrographs of the above sample are shown in FIG. 8. The 1cm x 2cm silicon substrate is covered with uniform silicon cone arrays. The density of the cones is measured as  $10^8/\text{cm}^2$ . The height of each cone is up to several microns and the lateral size of the cone tip ranges from tens of nanometers to hundreds of nanometers. The contrast of the cone body and cone tip appears to be different, suggesting  
10 different chemical contents. EDX microanalysis shows that the cone body is composed of silicon and the cone tip is composed of silicon and molybdenum (FIG. 9). Transmission electron microscopy (TEM) image shows different contrast of the cone body and cone tip (FIG. 10). Micro diffraction in FIG. 11 confirms that the cone body is single crystalline silicon (11a). The cone tip consists of several different  
15 material/material structures (11b,c,d): a silicon/molybdenum superlattice is observed right on top of the single crystalline silicon cone body, followed a polycrystalline molybdenum silicide, on top of which is a small amount of molybdenum metal.

### Example D

20 The silicon cone array for this sample was prepared under the same experimental conditions as example A, except that the angle between the center ion-beam and the substrate surface normal is 40 degree.

Cross-sectional SEM micrograph in FIG. 12 shows that the height of the cone is measured at ~6 microns, compared to that of example A (FIG. 13), which is  
25 measured as 4 microns, although their deposition time is the same.

### Example E

The silicon cone array for this sample was prepared under the same experimental conditions as example A, except that the substrate temperature is controlled at 400°C.

SEM micrographs of the above sample are shown in FIG. 14. The morphology of the cone in this sample is similar to that of example A, however, instead of single tip for each cone, double tip is observed. The contrast of the cone body and cone tip appears to be different and EDX microanalysis shows that the cone body is composed of silicon and the cone tip is composed of silicon and nickel. FIG. 15 shows the current-voltage (I-V) characteristics plot of the as-synthesized sample. The turn-on field is 27V/ $\mu\text{m}$ .

### Example F

The silicon cone array for this sample was prepared under the same experimental conditions as example A, except that the substrate temperature is controlled at 100°C.

SEM micrographs of the above sample are shown in FIG. 16. The morphology of the cone in this sample is similar to that of example A, however, instead of single tip for each cone, a multiple tip is observed. The contrast of the cone body and cone tip appears to be different and EDX microanalysis shows that the cone body is composed of silicon and the cone tip is composed of silicon and nickel. FIG. 17 shows the current-voltage (I-V) characteristics plot of the as-synthesized sample. The turn-on field is 18V/ $\mu\text{m}$ .

### Example G

In this example, the silicon cone array in example A was etched by hydrofluoric acid (HF). SEM micrograph (FIG. 18) shows the enlarged cone structures before (18a) and after (18b) the etching process. Fine cone tips with reduced lateral size are observed after HF etching. FIG. 19 shows the current-voltage (I-V) characteristics plot of the HF-etched sample. The turn-on field is  $14\text{V}/\mu\text{m}$ , which is considerably smaller than ( $34\text{V}/\mu\text{m}$ ) for the non-etched sample. In addition, time stability test at an emission current density of about  $35\text{ mA}/\text{cm}^2$  and over 15 hrs. shows no degradation of emission properties except for small fluctuations in current density.

### Example H

In this example, a low function metal-Cesium, was deposited on the silicon cone array in example F. FIG. 20 shows the current-voltage (I-V) characteristics plot of the as-synthesized sample. The turn-on field is considerably smaller at  $13\text{V}/\mu\text{m}$ .

### Example I

In this example, the sample in example A was put into a hot filament CVD chamber. Argon was introduced as protective gas atmosphere. The total pressure was maintained at 20 Torr during the growth process. The sample was heated up to  $950^\circ\text{C}$  for 5 minutes and then naturally cooled down.

SEM micrograph (FIG. 21) shows that single nanowire grows on the tip of individual silicon cone. TEM image shows that the diameters of the nanowires range from 50-100 nm (FIG. 22). Transmission electron diffraction (TED) pattern in FIG. 23 shows that the nanowires are amorphous. Electron energy loss spectroscopy

(EELS) confirms that the nanowires are composed of silicon (FIG. 24a) and oxygen (FIG. 24b). As the argon gas may contain certain amount of impurities, including oxygen, which leads to the oxidation of the silicon nanowires.

## 5 Example J

In this example, the nanowires growth conditions are the same as in Example I, except that hydrogen was introduced together with argon during the growth process. The argon/hydrogen ratio is 1:0.2. The morphology of the as-grown nanowires on the cone tips is similar to that in example I. TED pattern in FIG. 25 shows that the nanowires are crystalline silicon.

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